



Attorney Docket # 1978.EEM

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of Kevin Harris Becker Group Art Unit: 1712

Serial number: 10/016,844 Examiner: SELLERS, Robert E.

Filing date: 14 December 2001 Response date: 17 September 2004

Title: Dual Cure B-Stageable Adhesive for Die Attach

To: Commissioner for Patents
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

Sir: I, Kevin Becker, a citizen of the United States of America, currently residing at 18004 Cecelia Place, Cerritos, California 90703 declare as follows:

1. I am an inventor in the instant application and familiar with the issues raised in the Examiner's action on this application.

2. I graduated from Cornell University with a Bachelor of Science degree in Materials Science and Engineering and a Bachelor of Arts in Chemistry in 1989. I received a Ph.D. degree in Materials from the University of California, Santa Barbara, in 1995.

3. Since June 1999 I have worked at Ablestik Laboratories, a subsidiary of National Starch and Chemical Company. I currently hold the position of Business Scientist.

4. My experience has provided me with a strong knowledge of-polymer science and reactive chemistry.

5. The experiments below were conducted under my supervision and guidance to demonstrate that blended compositions as disclosed in US patent **6,187,416** to Satoh and US patent **5,081,167** to Jackson cure at the same temperature and do not anticipate or teach the dual cure chemistry of my invention.

6. A dual cure formulation as claimed in claim 1 of the instant patent application was prepared as follows:

Resin 1 – 30 parts liquid bismaleimide resin, 30 parts monomaleimide resin, 65 parts cinnamyl alcohol / dimer diisocyanate bis-carbamate, and 2.5 parts peroxide initiator (USP-90MD product from Crompton) were mixed together to form Resin 1.

Resin 2 – 40.27 parts rubberized epoxy oligomer, 15.04 parts trifunctional solid epoxy, 1.75 parts dicyandiamide and 0.50 parts amide accelerator were dissolved in 33.39 parts carbitol acetate solvent to form Resin 2 at 63.3% solids by weight.

Resin 1 (11.33 parts) was mixed with Resin 2 (90.95 parts). To this was added 7.5 parts fumed silica and 1.3 parts surfactants to form a B-stageable adhesive.

7. Limited by the availability of certain raw materials, **Satoh** Example 1 was reproduced as closely as possible, as shown in the chart below, and according to the directions as supplied in the Satoh patent. The choice of substitute materials for those not available is explained in the Comments.

Satoh, et.al. Example 1				
Components from Satoh, et.al., Example 1	Actual Materials Used to Reproduce Example	Description	Amount (parts)	Comments
Epoxy Solution:				
Epomic R-140	Epomic R-140	bis-A epoxy resin	15	
Epo Toho YDCN-704	Epo Toho YDCN-704	OCN epoxy resin	15	
Mirex XL-225	Mirex XL-CLL*	Epoxy resin hardener	30	*XL-225 Discontinued, XL-CLL is recommended replacement from same manufacturer - same chemistry
Curezol 2PZ	Curezol 2PZ	2-phenyl imidazole (accelerator)	0.6	
DMF	DMF	solvent	60.6	
		Subtotal:	121.2	
BMI Compound:				
Bis(3-ethyl-5-methyl-maleimidophenyl)methane	Matrimide-A from CIBA Chemical**	aromatic solid bis-maleimide resin	20	**Bis(3-ethyl-5-methyl-maleimidophenyl)methane is not commercially available - Matrimide-A is similar with the same chemistry
Polyethersulfone:				
product not specified - 1500 hydroxyl eq., 230C Tg	Radel A-104P	polyethersulfone	20	
NMP	NMP	solvent	90.3	
		Total:	251.5	
		Solid %:	40%	

Three minor changes were needed. The epoxy resin hardener used by Satoh is no longer available, so Mirex XL-CLL was substituted. It has the same chemistry as Mirex XL-225, but has a slightly different molecular weight and higher purity. The bismaleimide (BMI) used by Satoh is not commercially available, so a similar solid BMI resin was substituted. As Satoh did not specify the polyethersulfone used, a commercial product that fit Satoh's description was used. On my information and belief none of these changes should impact the fundamental chemistry behavior of the mixture.

8. Limited by the availability of certain raw materials, Jackson Example 1 was reproduced as closely as possible, as shown in the chart below, and according to the directions as supplied in the Jackson patent. The choice of substitute materials for those not available is explained in the Comments.

Jackson et.al. Example 1				
Jackson Raws	Equivalent Ablestik Raws	Description	Amount (parts)	Comments
Compimide 1206-R-60	Matrimide-A from CIBA Chemical*	Solid aromatic BMI resin	40	*Compimide 1206-R-60 could not be obtained. Matrimide-A is similar with the same chemistry.
DMF	DMF	solvent	26.67	
product not specified (Mn>500)	Epon SU-8	Bis-A novolac epoxy resin	10	
MEK	MEK	solvent	2.5	
cyanamide	cyanamide	Accelerator	2.75	
		Total:	81.92	
		Solid %:	64%	

Two minor changes were needed. The solid BMI resin used by Jackson could not be obtained, so a similar solid BMI resin was substituted. The bis-A novolac epoxy resin used by Jackson was not specified, so Epon SU-8, which fits Jackson's description, was selected. On my information and belief neither of these changes should impact the fundamental behavior of the mixture.

9. From each of the compositions prepared according to paragraph 6 (instant dual cure composition), paragraph 7 (comparative Satoh composition), and paragraph 8 (comparative Jackson composition) of this Declaration, adhesive films having a thickness of about 500um thick (wet) were prepared by casting onto 2 mil polyester release liner. The films were allowed to air dry for the following times:

Dual Cure paragraph 6:	2 hours
Comparative Satoh paragraph 7:	2 hours
Comparative Jackson paragraph 8:	20 min.

The films were then B-staged according to the B-stage profiles as specified in the cited references shown below:

Dual Cure paragraph 6:	30 min. @ 90C
Comparative Satoh paragraph 7:	5 min. @ 140C
Comparative Jackson paragraph 8:	3.25 min. @ 163C

Films were then cured according to the cure profiles recommended in the cited references shown below:

Dual Cure paragraph 6:	60 min. @ 175C
Comparative Satoh paragraph 7:	4 hours @ 200C
Comparative Jackson paragraph 8:	60 min. @ 180C

The resultant films were all approximately 100um thick after drying. Differential Scanning Calorimetry (DSC) was performed on each material at three different stages: a) before B-stage, b) after B-stage and c) after cure. The DSC charts are shown in Figures 1, 2 and 3 for Examples from Paragraphs 6, 7, and 8, respectively.

10. Thermosetting compositions undergo exothermic reactions when the resins contained in the composition undergo curing. DSC can be used to track these reactions. A DSC run before B-stage, that is, before curing, will show a separate exotherm as a peak in a graph for each reaction that occurs at a particular temperature. If multiple resins participate in the same reaction, there will be only one exotherm. If multiple resins participate in separate curing reactions, there will be multiple exotherms.
11. Figure 1a shows two exotherm peaks for Dual Cure paragraph 6. The first exotherm, associated with Resin 1, has a peak in the range of 150°-160°C and an enthalpy of reaction of 23.6 J/g, while the second exotherm occurs in the range of 190°-200°C and has an enthalpy of reaction of 23.7 J/g.
12. The comparative examples Satoh paragraph 7 and Jackson paragraph 8 have only one exotherm as seen in Figures 2a and 3a respectively. Comparative Jackson paragraph 8 does show some **endotherm** at lower temperatures, which is not associated with any resin curing, but rather is caused by solvent evaporation. This is only seen in Comparative Jackson paragraph 8, as Jackson,et.al. specified a short air drying time, which on my information and belief did not allow for all the solvent to fully evaporate.
13. A DSC run after B-stage for the Dual Cure paragraph 6 (the inventive sample) shows that the peak associated with Resin 1 in the system has completely disappeared, indicating that the first resin system is fully cured during B-stage. At the same time, the second, higher temperature exotherm peak associated with Resin 2 remains unaffected by the B-stage, indicating that Resin 2 remains completely uncured. In Figure 1b, it can be seen that only one exotherm remains for Dual Cure paragraph 6 after B-stage. The lower temperature peak has completely disappeared indicating that Resin 1 has completely reacted during B-stage. At the same time, the second peak remains unaffected; it still occurs between 190°-200°C and still has the same enthalpy of

reaction (38 J/g, which equals the original enthalpy divided by the solid content, as the solvent is evaporated during B-stage and thus no longer contributes to the weight of the sample – $24 \text{ J/g} / 0.63 = 38 \text{ J/g}$). This indicates that the Resin 2 cure was not initiated during B-stage.

14. This is quite different from the Satoh and Jackson art, which practices a **co-cure** of the various resins leaving a partially cured mixture. Looking at Figure 2a, it can be seen that Comparative Example paragraph 7 exhibits one exotherm between 170°-180°C with an enthalpy of approximately 100J/g. After B-stage (Figure 2b) there is still one peak, but the peak has significantly shifted down to below 160°C and the residual enthalpy of reaction is only 46 J/g. This indicates that both the BMI and epoxy resins are co-curing, and that during B-stage **both** resins are being partially cured. Likewise, Figure 3a shows that Comparative Example paragraph 8 exhibits only one exothermic peak at 170°-180°C with an enthalpy of 226 J/g. After B-stage, the peak has not shifted, but the enthalpy of reaction is only 113 J/g, indicating that the mixtures have been partially cured during the B-stage.

15. In my opinion, the above examples serve to illustrate the difference **chemically** between the co-curing compositions disclosed in the cited art and the compositions in the present patent application.

16. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by a fine or imprisonment or both under 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

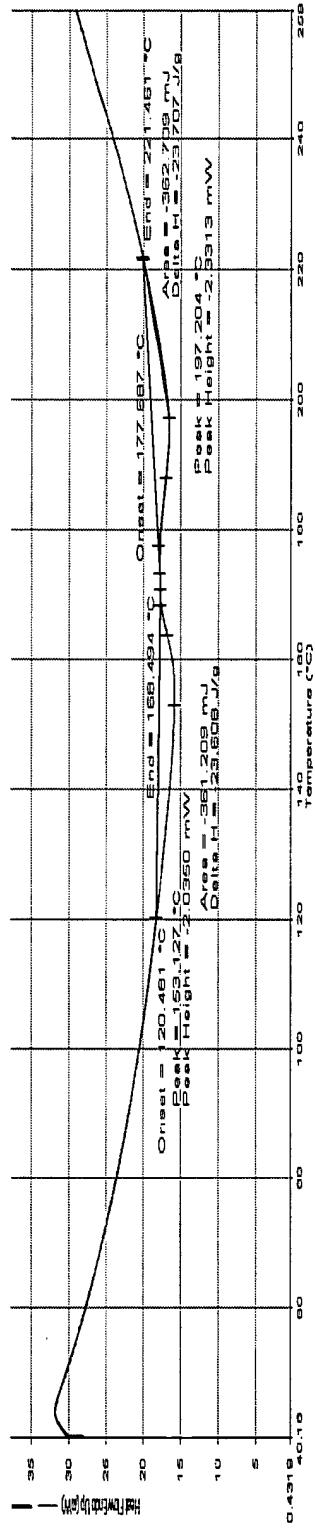
Signed at Rancho Dominguez, California, this 23 September 2004



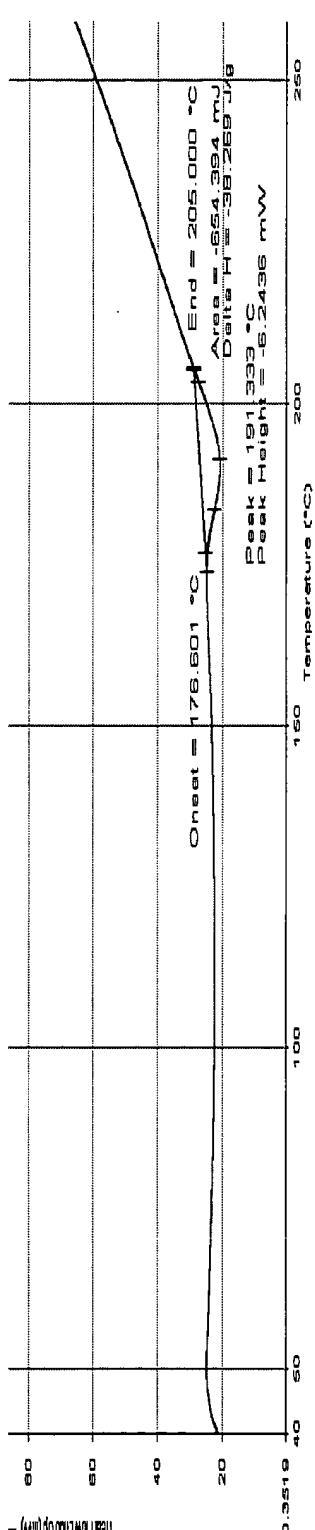
Kevin Becker

Figure 1 – Dual Cure Inventive Example

a) DSC of air dried film – no heat history



b) DSC after B-stage of 30 min. @ 90C



c) DSC after cure of 1 hour @ 175C

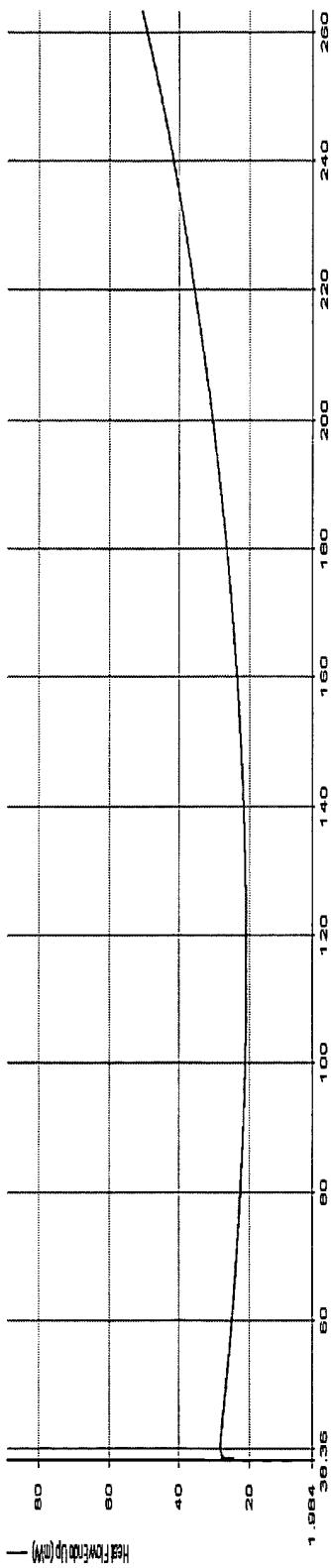
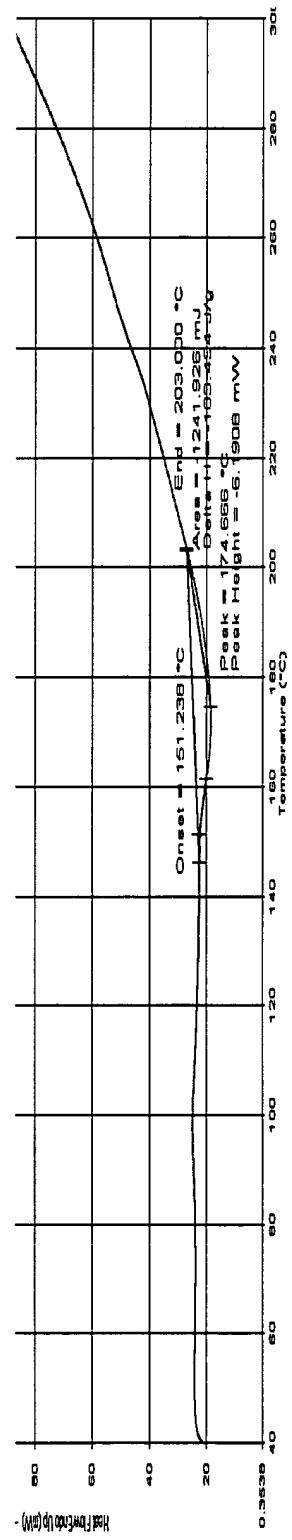
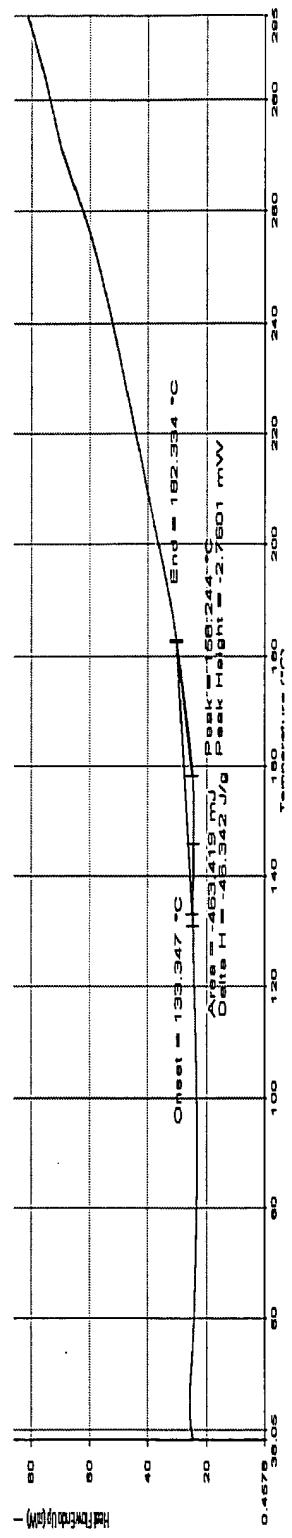


Figure 2 - Satoh, Example 1

a) DSC of air dried film – no heat history



b) DSC after B-stage of 5 min. @ 140C



c) DSC after cure of 4 hours @ 200C

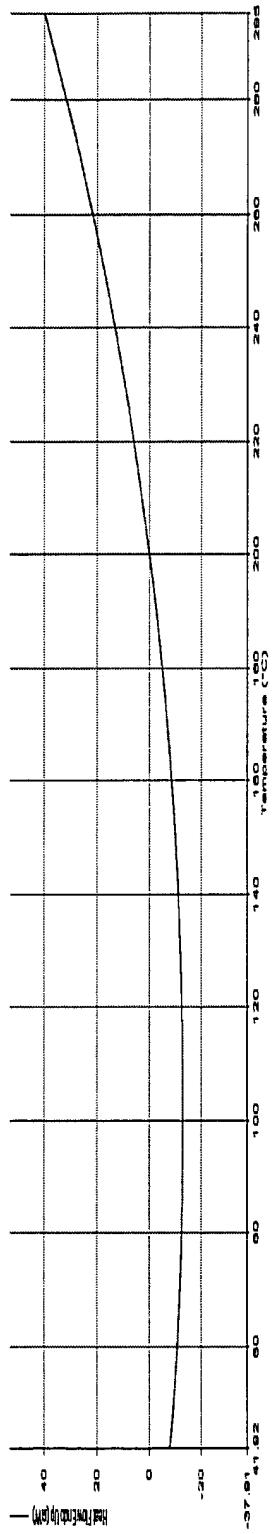
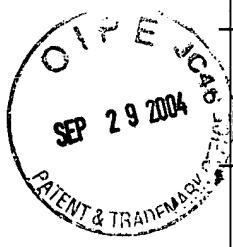
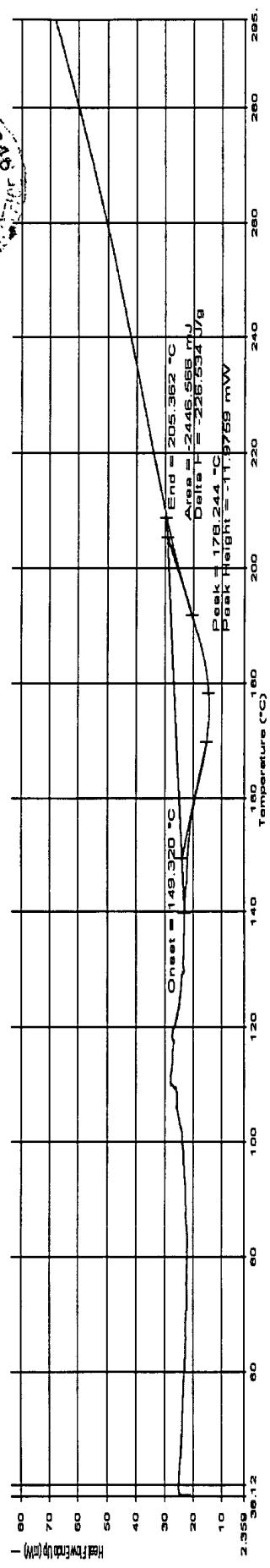


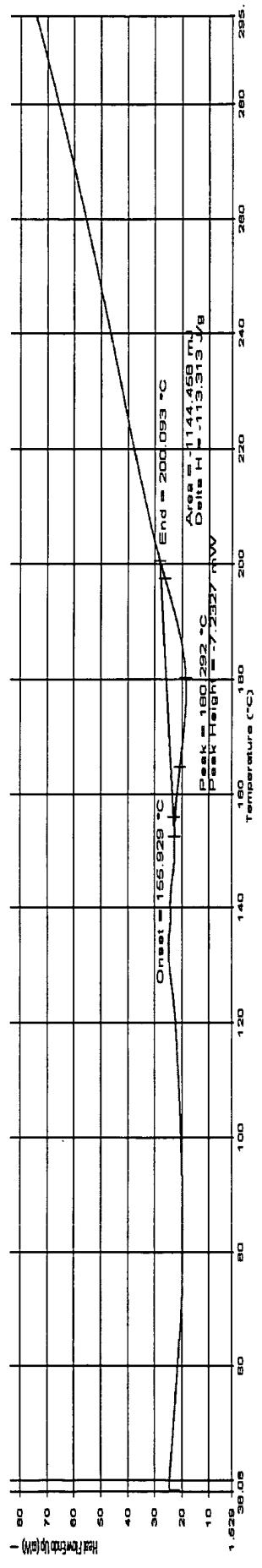
Figure 3 - Jackson, Example 1



a) DSC of air dried film – no heat history



b) DSC after B-stage of 3.25 min. @ 163°C



c) DSC cure of 1 hour @ 180°C

